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The Production of Free Lime in Portland Cement by Heating.*

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OF THE BUILDING RESEARCH STATION.

THE results reported by Dr. G. A. Ashkenasi in the February and March numbers of CEMENT AND CEMENT MANUFACTURE on the increase in the free lime content of cements on heating at 1,000 deg. C. are in agreement with the earlier results reported by S. L. Meyers¹ and by E. T. Carlson², and with unpublished work carried out at the Building Research Station.

Carlson showed that tricalcium silicate tends to dissociate into dicalcium silicate and lime at temperatures between 1,000 and 1,300 deg. C. The amount of decomposition of pure $3\text{CaO} \cdot \text{SiO}_2$ was stated to be very small even with long periods of ignition, but is increased very markedly by the presence of either of the products of decomposition, i.e., by CaO or $2\text{CaO} \cdot \text{SiO}_2$, and also by gypsum. The optimum temperature of decomposition was found to be about 1,175 deg. C., at which temperature the rate of decomposition is about fifteen times as great as at 1,000 deg. C.

Some similar work was carried out at the Building Research Station on the rate of liberation of lime from commercial Portland cements and cement clinker prior to the publication of the work of Carlson. The glycerol-ammonium acetate method of estimation of free lime was used, and ignitions were carried out in electric tube furnaces. The earlier experiments were confined to materials ignited at temperatures up to 900 deg. C. In Table I are shown the free lime contents, before and after ignition, of a number of different Portland cements and Portland cement clinkers (Nos. 1 to 8). No increase in free lime content on ignition is observed at 550 deg. C., but there is a very pronounced increase at 900 deg. C. and a lesser one at 700 deg. C. The amount of free lime liberated on ignition varies considerably with the different cements, which include both normal and rapid-hardening varieties. In general, cements with the higher free lime content before ignition develop it to a greater extent during ignition. The two clinkers Nos. 6 and 7 in the Table both show no real increase in free lime content after ignition, whilst No. 8 which has a high free lime content initially shows an appreciable increase.

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¹ Meyers, S. L., *Rock Products*, 1930, 33 (8) 78.

² Carlson, E. T., *Rock Products*, 1931, 34 (25) 52; *Bureau of Standards Jour. Research*, 1931, 7, 893.

In order to confirm that the presence of gypsum influenced the decomposition clinkers Nos. 6 and 7 were ground with gypsum and tested as before by ignition at 900 deg. C. The results are shown in the Table (Nos. 9 and 10). In one case the increase in free lime content on ignition is very small, whilst in the other it is large. The results of these two tests agree with those found with actual cements in that the sample with higher free lime content shows the great effect on ignition. Clinker No. 8 was reburnt at 1,500 deg. C. and then heated for six hours at 900 deg. C. The free lime was completely removed by ignition at 1,500 deg. C., and none was developed during the subsequent heating at 900 deg. C. (No. 11). A portion of this clinker, after reburning at 1,500 deg. C., was reground with gypsum and tested. It has no free lime before ignition at 900 deg. C. and less than 1 per cent. after ignition (No. 12).

From these results it would appear that to obtain an appreciable rate of dissociation of the tricalcium silicate in cements at 900 deg. C. both gypsum and free lime must be present together. This was confirmed by the results given in Nos. 9, 13 and 14 of the Table, in which is shown the effect of adding to clinker No. 6 gypsum alone, lime alone, and gypsum and lime together, respectively.

TABLE I.
EFFECT OF IGNITION ON FREE LIME CONTENT OF PORTLAND CEMENTS.

Sample No.	Material.	Treatment.	Free lime content (per cent.)		Increase in free lime content on ignition.
			Before ignition.	After ignition.	
1	Cement	Hours. Deg. C.			Per cent.
		6 at 550	1.6	1.8	0.2
		2 at 700	—	4.0	2.4
		1 at 900	—	4.5	2.9
2	Cement	6 at 900	—	11.7	10.1
		6 at 550	3.8	3.8	0.0
		1 at 900	—	8.2	4.4
		6 at 900	—	13.2	9.4
3	Cement	6 at 900	0.1	5.9	5.8
4	Cement	6 at 900	0.8	4.0	3.2
5	Cement	6 at 900	3.0	11.8	8.8
6	Clinker	6 at 900	Nil	0.1	0.1
7	Clinker	6 at 900	2.0	2.2	0.2
8	Clinker	6 at 900	4.6	8.3	3.7
9	Clinker No. 6 + 4.3 per cent. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$..	6 at 900	0.2	0.9	0.7
10	Clinker No. 7 + 4.3 per cent. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$..	6 at 900	2.8	10.1	7.3
11	Clinker No. 8 reburnt at 1,500 deg. C. ..	6 at 900	Nil	Nil	0.0
12	Clinker No. 8 reburnt at 1,500 deg. C. + 4.3 per cent. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$..	6 at 900	Nil	0.8	0.8
13	Clinker No. 6 + 2.0 per cent. CaO	6 at 900	2.7	2.8	0.1
14	Clinker No. 6 + 4.3 per cent. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + 2.8 per cent. CaO ..	6 at 900	2.7	8.9	6.2
15	Clinker No. 6	46 at 1,150	Nil	9.4	9.4
16	Clinker No. 6 + 4.3 per cent. $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$..	46 at 1,150	0.2	12.6	12.4

The optimum temperature for decomposition was found by Carlson (*loc. cit.*) to be about 1,150 deg. C., and a sample of clinker No. 6 was therefore ignited at

this temperature. Over 9 per cent. of free lime was liberated (No. 15) in contrast to the zero value obtained at 900 deg. C. (No. 6). A mixture of this clinker and gypsum heated at 1,150 deg. C. gave a still higher value (No. 16).

The above experiments show that the decomposition of tricalcium silicate in Portland cement takes place at temperatures down to about 700 deg. C. No decomposition was observed on heating for six hours at 550 deg. C. on any cement, but it is possible that it might take place at that temperature, or even lower, if the time of heating were sufficiently extended. Some cement clinkers show decomposition at 900 deg. C., although to a lesser extent than the cements, whilst other cement clinkers show no decomposition at that temperature. This is probably attributable to the differing contents of free lime and sulphur trioxide in the clinkers, since the addition of lime and gypsum together greatly accelerates the decomposition.

It appears from these results, together with those of Carlson and Ashkenasi, that tricalcium silicate in cements is entirely unstable below about 1,350 deg. C., but that its decomposition only takes place with any observable velocity above about 1,050 deg. C. when heated alone, and above about 600 deg. C. in the presence of catalysts such as free lime and gypsum.

British Standard Specification for Portland-Blastfurnace Cement.

The British Standards Institution has issued a revised edition of the B.S. Specification for Portland-Blastfurnace Cement (B.S. Specification No. 146-1932), the last revision of which took place in 1926. The new edition is required owing to the recent revision of the B.S. Specification for Portland Cement, and the changes introduced bring the physical tests in the two specifications into exact agreement.

A summary of the alterations is given in the Foreword to the Specification, amongst which the following may be specially noted: The neat cement test is not now an obligatory requirement. The 28-day mortar test has been eliminated, a new 3-day test being inserted so that the periods for the tensile tests on cement and sand are 3 and 7 days. With the object of making the testing more independent of the judgment of the operator, the quantity of water required for preparing the neat-cement paste or cement-and-sand mortar is determined by a modification of the Vicat plunger method, the percentage of water necessary to produce a prescribed settlement of the plunger into a pat of neat cement being multiplied by a factor: convenient tables are given for obtaining without calculation the required percentages. The appropriate British Standard wire cloths for test sieves are substituted for those previously specified. Copies of the specification may be obtained from the British Standards Institution, 28, Victoria Street, London, S.W.1, price 2s. 2d. by post.

Licensing of Machinery.

The Import Duties Advisory Committee announce that they are now open to receive applications in connection with the scheme authorised by Section 10 of the Finance Act, 1932, for the exemption of particular consignments of machinery (being machinery of a kind not for the time being procurable in the United Kingdom) from the whole or part of the duties chargeable under the Import Duties Act, 1932. The classes of machinery in regard to which application for exemption may be made include weighing, packing and filling machinery. Application may be made by a firm purchasing machinery for its own use, or by an importer having the sole agency for the sale of a particular machine in this country. Forms of application may be obtained on request in writing from the Import Duties Advisory Committee, Caxton House (West Block), Tothill Street, Westminster, S.W.1.

The Hardening of Portland Cement.

By F. F. TIPPMMANN.

IN the January 1932 number of CEMENT AND CEMENT MANUFACTURE appeared Professor H. Kühl's criticism of my article of October 1931, together with my reply and further comments by Professor Kühl. The following remarks are presented in the hope of concluding this discussion:

(1) In Professor Kühl's 1912 lecture on lime and gypsum expansion, he spoke of the "fact" that considerable quantities of calcium hydrate are formed on the hydration of even the best sound Portland cement, and can easily be seen on microscopic examination of hardened mortar in the form of hexagonal tables." He was admittedly premature in speaking of the "fact," just as he is now premature in regarding as a "fact" the existence of the more than hypothetical calcium hydrosilicate, which as yet has been seen by nobody.

In the meantime Dr. H. W. Gonell (Berlin-Dahlem) has convinced himself of the presence of large numbers of $\text{Ca}(\text{OH})_2$ crystals in the form of somatoid lamellæ in a Portland cement preparation which I sent to him. I should like to take this opportunity of thanking Dr. Gonell for his friendly collaboration.

(2) With regard to the specific gravities of the two modifications of calcium hydrate, I have not professed to speak the last word. I have merely endeavoured to bring nearer the final solution of this important technical and scientific problem. The investigation is obviously one for the pure scientist to undertake.

However CaO is slaked or hydrated, the resulting amorphous hydrate does not correspond accurately to the formula $\text{Ca}(\text{OH})_2$, but always contains an excess of loosely combined water. Only on drying the amorphous hydrate to constant weight at 100–105 deg. C. does it accurately correspond to the formula, and determinations of specific gravity must be carried out with such material.

Finally, there exist a number of substances which, although they possess exactly the same formula, exist in several modifications which have different specific gravities.

(3) The detailed instructions which I gave to enable my results to be checked are not new, but are simply given in great detail for the first time.

Since the publication of my first article Dr. F. Quast (Karlshorst) has informed me of certain statements in the literature which are related to my observations. Thus on p. 354 of Feichtinger's "Chemical Technology of Mortar Materials," dealing with Schott's cement, is the passage: "In agreement with this Schott also found that gypsum has no effect on lime which is instantaneously slaked by water. On the contrary, with slowly slaking limes on which gypsum has time to exert its effect the slaking is considerably delayed, with diminution of the accompanying phenomena of swelling and evolution of heat. This result can be attained by slaking with a saturated gypsum solution. On adding more gypsum than can be dissolved by the water used, a second phenomenon accompanies the weakening of slaking, viz., a capacity for hydraulic hardening, or hardening under the sole influence of water and with exclusion of carbon dioxide; such hardening does not occur with the usual slaked lime." I have no experience of an "instantaneously" slaking lime; the shortest time I have observed before the commencement of slaking is three minutes in the case of pure lime. Nevertheless saturated gypsum solution exerted its entire effect on the limes I have studied, and completely eliminated the slaking process.

(4) It is my belief that in the near future there will be surprising developments in research on the hydration of Portland cement, and in particular that the colloidal theory of hardening will be eclipsed.

Dr. Guttman's paper read before the Kaiser Wilhelm Institute for Research on the Silicates in November, 1931, on the setting of tricalcium silicate (which is quite definitely the alite of clinker) has already dealt a severe blow to the colloidal theory by indicating that crystalline calcium hydrate plays a most important part in hardening.

Further, there already exist sufficient practical experimental data to compel the complete recognition of the role of crystalline calcium hydrate, among which I need only briefly cite the following:

(a) Hardened Portland cement, burnt to clinkering in the form of small pieces, gives an extremely hot and expansive cement. If, on the other hand, it is finely powdered before burning the cement is quite normal and sound. The lime in the hardened cement is thus present as free hydrate crystals. When the lime in the set cement burnt in small pieces is determined by the glycerine method we get an estimate of the quantity of hydrate deposited in crystal form which scarcely allows any possibility for the existence of the hypothetical calcium hydrosilicate.

(b) If hardened crushing test-pieces are heated in dry air to temperatures of 100, 200, 300, 400, 450 and 500 deg. C. it is surprising how rapidly the strength increases with the temperature of heating up to 450 deg. C., and only sinks to almost zero between 450 and 500 deg. Thus it is the thermal dissociation of calcium hydrate (beginning at about 450 deg.) which completely destroys the strength. If, therefore, the decomposition of the hydrate causes loss of strength, the hydrate must logically be the main cause of strength (hardening).

If, in accordance with the colloidal theory, the hypothetical calcium hydrosilicate (considered to be a chemical compound) be the source of strength, then strength must disappear with only slight increase of temperature. In reality there is a considerable increase in strength with temperature. The second most important factor in the strength of cement can, however, be pure silica gel, whose strength greatly increases with temperature, *i.e.*, with increasing loss of liquid. The liquid in cement remains constantly supersaturated with calcium hydrate as temperature increases, so that the crystalline hydrate can continue to separate until its dissociation temperature is reached.

(c) The most finely ground Portland cement (so fine that hydration is rapidly complete), hardened for 180 days and dried at 120 deg. C. to constant weight, gives a loss on ignition (water) closely corresponding to the amount of water necessary completely to hydrate the total amount of lime in the cement, *viz.*, about 21 per cent.

(d) Suppose two cements are prepared from the same raw materials and under exactly similar conditions, and are further ground to the same fineness and are both sound. Suppose also that they are of the same chemical composition except as regards lime content, but that the lime contents are 64 and 66 per cent. respectively. It will be found that after a defined time the 64 CaO cement will give a crushing strength of 4,250 lb. per sq. in. and the 66 CaO cement 8,500 lb. Exactly the same quantity of the hypothetical calcium hydrosilicate must have formed in the two cases, so that the high strength of the second cement must be due entirely to the action of the increased lime content of only 2 per cent. This, however, can only contribute to hardening in the form of hydrate. If so small an amount of lime can exert so great an effect, is it not reasonable to accept that hardening is almost entirely to be attributed to calcium hydrate? This example is in complete agreement with practice.

I have analyses of the well-known rapid-hardening Thyssen cement, and will consider the chemical composition in conjunction with the 7-days' strengths :

	Per cent. SiO ₂	Per cent. CaO	7-Day crushing strength. lb. per sq. in.
Portland Cement	23.31	65.01	4,250
Rapid-hardening Cement ..	20.84	67.21	8,500

The effect of calcium hydrate in hardening is unequivocally seen from these figures. Although a smaller amount of calcium hydrosilicate must be formed with the rapid-hardening cement, yet its strength is 100 per cent. higher. Thus, even though the disputed hydrosilicate should actually exist, it can have no great importance in hardening. On the other hand, these data can be explained on my theory of hardening : the smaller quantity of silica gel is much more rapidly dehydrated by the formation of the increased quantity of calcium hydrate crystals,

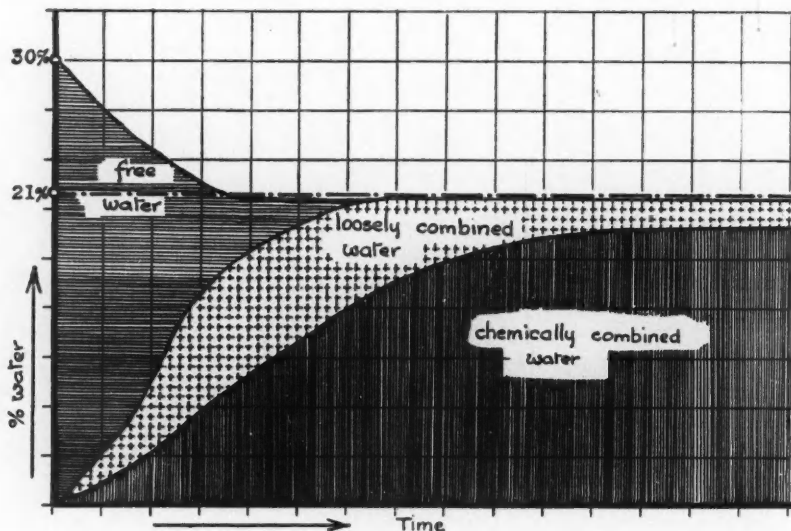


FIG. 1

which results in the increased strength. These four instances should alone be sufficient to satisfy us that crystalline calcium hydrate plays the chief part in hardening.

(5) An exact proof that pure silica gel—and not an amorphous calcium hydrosilicate—is formed on hardening has not yet been brought forward. Since, however, the alleged hydrosilicate can even be split up into its components by pressure, it appears very doubtful whether it can be considered to be a chemical compound. It is much more probably a mixture of silica and calcium hydrate, and as such completely fits in with my theory.

The dehydration curve of tricalcium silicate given by Krauss in the *Protokoll* of the Association of German Portland Cement Manufacturers for 1929 (p. 170)

completely agrees with my conceptions. The curve more recently given for hydrated tricalcium silicate in *Zement** is, however, very broken up, while the water is insufficient for the hydration of three molecules of CaO. Krauss's painstaking researches are to my mind in error in that the time of duration of the experiments was much too long. Great variations in the conditions of combination of the water must certainly have occurred during the three months of an experiment, with the result that the dehydration curve shows hardly any breaks capable of interpretation.

The progress of combination of water with time of hardening must proceed approximately as shown in Fig. 1.

Portland cement mixed with 30 per cent. water will at first only contain free water. Very soon, however, part of the water will be loosely combined in the gel and part chemically combined as calcium hydrate crystals. The free water is rapidly reduced by evaporation to a minimum of 21 per cent. total water, which practically corresponds to the quantity capable of chemical combination with the whole of the lime. The loosely-combined water reaches a maximum and then steadily diminishes in favour of chemically-combined water. The curves of loosely and chemically-combined water have no common point, and in very old mortar proceed asymptotically. The ideal of completion of hardening would correspond to a common point, but in practice this is never attained.

(6) I hope shortly to publish a short description of the new mono-binocular-stereo-microscope, which is best suited to the investigation of hardened mortar. This is an excellent instrument, capable of finally converting all adherents of the colloidal theory of hardening.

To summarise, I can only confirm that the existence of calcium hydrosilicate is not the "fact" of which Professor Kühl speaks, but is purely an assumption.

*Krauss and Jörns. *Zement*, Vol. 20, p. 317, 1931.

German Cement Companies' Reports.

Portland-Cementwerke Heidelberg-Mannheim-Stuttgart A.G. reports a net profit of RM. 1,087,000 (£54,350) for 1931 and a dividend of 4 per cent. The net profit for 1930 was RM. 2,070,000 (£103,500) when a dividend of 7 per cent. was paid.

Portland-Cementwerk Burglengenfeld A.G. has declared a dividend of 4 per cent. for the year 1931 with a net profit of RM. 4,813 (£240). This compares with a dividend of 7 per cent. in 1930 when the net profit was RM. 91,000 (£4,550).

Alsen'sche Portland-Cementfabriken passed its dividend for 1931, when the trading profit was RM. 719,484 (£35,974). A dividend of 7 per cent. was paid in 1930 when the trading profit was RM. 1,378,357 (£68,917).

Vereinigte Harzer Portland-Cement und Kalkindustrie passed its dividend for 1931, when the net profit was RM. 46,000 (£2,300). This compares with a net profit of RM. 156,000 (£7,800) in 1930 when a dividend of 5 per cent. was paid.

Portland-Cementfabrik Hemmoor has passed its dividend for the year 1931; a dividend of 10 per cent. was paid for the year 1930.

Portland-Cementfabrik "Germania" A.G. passed its dividend for 1931 when there was a net loss of RM. 225,331 (£11,266). A dividend of 7 per cent. was paid for 1930 when there was a net profit of RM. 516,930 (£25,846).

Portland-Cement-und-Kalkwerke "Anna" A.G. reports a loss of RM. 30,193 (£1,509) for the year 1931, compared with a loss of RM. 26,321 (£1,316) for 1930.

Behaviour of Portland Cement when Heated.

By Dr. GABRIEL A. ASHKENASI

(CHIEF CHEMIST, PORTLAND CEMENT CO. "NESHER," LTD., PALESTINE.)

By the estimation of uncombined CaO in Portland cement by means of the glycerol-tartaric acid method it has been observed that a considerable quantity of calcium oxide is evolved from Portland cement after several hours' heating at 1,000 deg. C. This quantity increases with the time of ignition, and after a certain period of heating reaches its maximum. This decomposition of Portland cement has already been described in cement literature.

M. E. Leduc, for example, presented a paper in 1901 at the Congress of Building Materials in Budapest upon the dissociation of cement under the action of a temperature of about 1,000 deg. C. He described how he heated cement in a platinum capsule at 950 to 1,000 deg. C., and then extracted the liberated lime by boiling the heated cement with a 10 per cent. solution of sugar in water. After 15 minutes' boiling the mixture was filtered and the filtrate titrated for CaO with a standard sulphuric acid. The results obtained showed that the quantity of lime set free increases with the time of heating. M. Leduc used the 10 per cent. solution of sugar in water for the detection of uncombined lime, which decomposes every Portland cement. If one tries to estimate the proportion of free CaO in Portland cement by the use of a solution of sugar in water one arrives at false conclusions. For example, a Portland cement tested by the glycerol-tartaric method showed no traces of free CaO, but the same Portland cement, after boiling for 15 minutes with a 10 per cent. solution of sugar in water, filtered, the filtrate, when tested for CaO, showed 3.92 per cent. of liberated CaO. Therefore, Leduc's assumption, although correct in principle, could not at that time be proved by his method.

Modern methods of estimation of uncombined lime prove in a more incontestable manner this decomposition of Portland cement.

As stated in CEMENT AND CEMENT MANUFACTURE for February and March, 1932, weil-burnt clinker, when ground to a fineness of zero per cent. residue on the sieve of 10,000 meshes per square cm. and then tested for uncombined CaO, showed 0.45 per cent. residue. The same cement when ignited at 1,000 deg. during many hours increases its proportion of free CaO to 9.32 per cent. It was also observed that the period of heating depends on the quality of cement clinker. The more sharply sintered clinkers require a longer period of heating to reach a maximum of evolved free lime than the less sharply sintered ones. Further, it was noticed that the presence of gypsum accelerates this dissociation, in contrast with some chemical compounds which retard this process, of which tricalcium phosphate proved to be an example.

The comparative tests of pure cement and cements with 5 per cent. CaSO₄ and 5 per cent. Ca₃PO₄ gave the following results. The chemical composition of the cement used for testing was: Loss on ignition, 1.02 per cent.; silica, 21.10 per cent.; alumina, 6.11 per cent.; ferric oxide, 3.36 per cent.; calcium oxide, 66.45 per cent.; magnesia, 1.00 per cent.; sulphuric anhydride, 0.60 per cent.; alkalis and loss, 0.36 per cent.

Samples of this cement without gypsum, with 5 per cent. gypsum, and with 5 per cent. of tricalcium phosphate were put in platinum crucibles and heated for several hours at 1,000 deg. C. in an electrical muffle furnace. From time to time portions of 1 gr. of weight were taken and tested for CaO content by the glycerol tartaric acid method.

Time of Ignition.	Percentage of CaO Detected in Cement.		
	Pure Cement.	With 5 per cent. gypsum.	With 5 per cent. tricalcium phosphate.
2 hours	1.83	—	—
4 "	2.18	4.47	—
8 "	3.44	9.54	—
24 "	4.54	9.61	9.74
48 "	5.81	—	2.81
100 "	9.31	—	3.81

These comparative results show distinctly the retarding effect of tricalcium phosphate and the accelerating action of gypsum on the decomposition of cement.

Portland cement changes its properties after being ignited. Its colour becomes paler, with a tinge of yellow, and it loses its qualities as a hydraulic hardening material.

Portland cement of the chemical composition

Loss on ignition	2.02 per cent.
SiO ₂	20.94 " "
Al ₂ O ₃	6.01 " "
Fe ₂ O ₃	3.05 " "
CaO	65.66 " "
MgO	1.04 " "
SO ₃	0.42 " "
Loss and alkalis	0.86 " "

had been heated for 70 hours at 1,000 deg. C. The changes of its qualities after heating are given below.

TABLE I.

	Before Ignition.	After 70 Hours' Ignition.
Percentage of uncombined lime detected by the glycerol-tartaric acid method.	0.22 per cent. (average of two tests).	11.81 per cent.
Boiling tests for soundness	Set hard without cracks or shrinkage.	Completely disintegrated.
Le Chatelier tests for soundness ..	1 mm. expansion after 6 hours' boiling.	After 4 hours' immersion in cold water an expansion of 51 mm., when boiled completely disintegrated.

TESTS FOR TENSILE STRENGTH.

(1 part cement and 3 parts standard sand.)

(a) Briquettes stored 1 day in damp atmosphere and 6 days in water.	Average of test of 6 briquettes: 607 lb. per in. ²	43 lb. per in. ²
(b) Briquettes stored 1 day in damp atmosphere and 6 days in air.	Average of test of 6 briquettes: 547 lb. per in. ²	120 lb. per in. ²

The same cement, after 70 hours' ignition, was aerated for several days. Every day the cement was mixed thoroughly, and samples of 1 gr. of weight were taken and examined for uncombined CaO. The results of the examination were as follows: After one day, 10.03 per cent. of CaO was found; after three days 6.48 per cent. of CaO was found; after seven days 0.74 per cent. of CaO was found; after ten days traces of CaO were found.

Standard briquettes (1:3) were prepared and tested for tensile strength seven days after gauging. In spite of absence of "free lime" in this sample, the briquettes showed an average tensile strength of 50 lb. per square inch only. Le Chatelier cylinders, after immersion in cold water for 24 hours, did not show any expansion, but disintegrated completely on boiling.

The next step was to try to separate the ingredients of the cement decomposed by heating. Ten grs. of the ignited cement were intimately mixed by rubbing with 100 c.cm. glycerol of 1.262 sp.g. The pulp obtained was washed with 300 c.cm. methanol in an Erlenmeyer flask. After being well shaken, the muddy mixture was boiled for four minutes, left for several hours, and then filtered off. [It is advisable to filter under a bell jar with a water-absorbing material (P_2O_5 for example) to prevent the influence of humidity.] The precipitate was well washed with a solution of glycerol in methanol, and then with methanol only. The filtrate obtained was reduced to 500 c.cm.

Fifty c.cm. of this filtrate, corresponding to 1 gr. cement digested, were taken, diluted with 100 c.cm. water, heated to boiling, and titrated with 0.1 N. hydrochloric acid and phenolphthalein as indicator. The results of three titrations were as follows:

		c.cm. of 0.1 N. HCl.	Gr. of CaO.
(1)	40.60	0.1136
(2)	40.75	0.1141
(3)	40.50	0.1134

An average of 11.37 per cent. of CaO was found. One hundred c.cm. of the same filtrate were evaporated to dryness in a platinum dish and then ignited to destroy the organic substances. The completely white residue was dissolved in strong hydrochloric acid, the solution made alkaline with ammonia, and CaO determined with ammonium oxalate in the usual way.

As an average result of two analyses, 11.61 per cent. CaO was detected. The direct estimation of CaO in the same cement by means of the glycerol-tartaric acid method gave 11.81 per cent.

The estimation of uncombined lime in Portland cement by the glycerol-tartaric acid method is based on the empirically found equivalent 1 c.cm. 0.1 N. tartaric acid = 0.0036 gr. CaO.* The examination of the filtrate containing uncombined lime digested from decomposed cement showed results as 11.37 per cent. and 11.61 per cent. respectively, which prove the correctness of the glycerol-tartaric acid method.

The residue obtained by the digestion of ignited cement with glycerol and methanol was analysed. The results of analysis were as follows:

SiO ₂	24.40	per cent.
Al ₂ O ₃	7.46	" "
Fe ₂ O ₃	3.44	" "
SO ₃	0.67	" "
MgO	1.46	" "
CaO	61.32	" "
Loss and alkalis	1.25	" "

* CEMENT AND CEMENT MANUFACTURE, 1932, No. 2, p. 64.

When this residue was heated for a second time to 1,000 deg. C. for 24 hours and then tested for free lime it gave a negative result. No traces of CaO could be detected.

A photomicrograph of this residue is given in Fig. 1. For comparison the same Portland cement, not heated, was digested in the same way with glycerol and methanol. The filtrate obtained showed traces of CaO only, and is reproduced in Fig. 2. Whilst the crystals in the cement which had not been heated remained unchanged, the crystals of the heated cement have the appearance of being destroyed.

Considering the results of analysis of the residue obtained by digestion of cement heated for 70 hours to 1,000 deg. C., it can be concluded that its composition corresponds to a substance which is composed of a bicalcium silicate, tricalcium aluminate, and bicalcium ferrate. [For the sake of simplicity it is

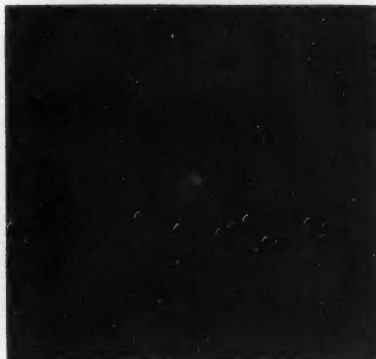


Fig. 1.

Photograph of Portland Cement heated for 70 hours and then digested with Glycerol and Methanol.

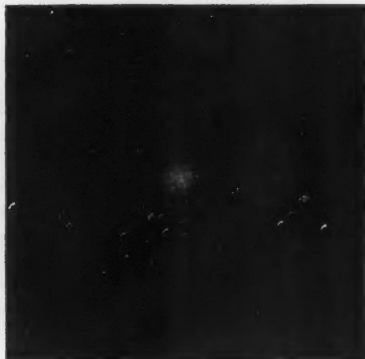


Fig. 2.

Photograph of Portland Cement not heated, after digestion with Glycerol and Methanol.

assumed that iron oxide combines with calcium oxide to bicalcium ferrate, although it is supposed that this oxide forms with more complicated CaO compounds.]

Theoretically 1 mol. SiO_2 requires 112.2 gr. CaO

1	„	Al_2O_3	„	168.3	„	„
1	„	Fe_2O_3	„	112.2	„	„
1	„	SO_3	„	56.1	„	„

For the proportions obtained by the analysis of this residue the corresponding quantities of CaO were: For 24.4 parts by weight of SiO_2 , 45.3 per cent. CaO, for 7.46 parts by weight of Al_2O_3 , 12.55 per cent. CaO; for 3.44 parts by weight of Fe_2O_3 , 2.42 per cent. CaO; for 0.67 parts by weight of SO_3 , 0.47 per cent. CaO. The total amount of CaO according to this calculation is equal to 60.74 per cent. We had detected in our residue 61.32 per cent. CaO, a quantity which coincides well with the calculated theoretical one.

An examination of another cement of a composition

Loss of ignition	1.63 per cent.
SiO ₂ (soluble)	20.04 " "
" (insoluble)	0.23 " "
Al ₂ O ₃	5.96 " "
Fe ₂ O ₃	3.01 " "
CaO	65.51 " "
MgO	0.88 " "
SO ₃	2.61 " "
Loss and alkalis	0.13 " "

showed a similar result. This cement contained a considerable amount of gypsum. After heating for 8 hours to 1,000 deg. C. a maximum of CaO set free had already been obtained. The digestion of this cement after ignition with glycerol and methanol produced a residue the composition of which was as follows (the analysis had been executed on a sample ignited till constancy of weight was obtained):

SiO ₂ (soluble)	23.62 per cent.
" (insoluble)	0.20 " "
Al ₂ O ₃	6.85 " "
Fe ₂ O ₃	3.60 " "
CaO	60.83 " "
MgO	1.21 " "
SO ₃	2.93 " "
Loss and alkalis	0.76 " "

The theoretical figures for the proportions detected in this residue are as follows: For SiO₂, 43.98 per cent. CaO; for Al₂O₃, 11.18 per cent. CaO; for Fe₂O₃, 2.53 per cent. CaO; for SO₃ to form gypsum, 2.02 per cent. CaO.

The theoretical quantity of the total CaO required to form bicalcium silicate, tricalcium aluminate, and bicalcium ferrate totals 57.69 per cent. CaO. When the quantity of CaO required to form gypsum is subtracted from the amount of CaO detected in this residue in this case also a figure is obtained which coincides nearly with the calculated one.

It is proved that cement decomposes by heating to 1,000 deg. C. The products of this decomposition are free lime and an aggregate which is probably composed of bicalcium silicate, tricalcium aluminate, and bicalcium ferrate.

The question of the compounds in cement and the formation of cement clinker has up to the present not been definitely solved. Especially, it is not clear whether there is present in cement a tricalcium silicate as a chemical compound, or whether a bicalcium silicate forms with CaO a solid solution. For many reasons the formation of tricalcium silicate by the conditions of cement burning does not seem convincing. Dr. W. Dyckerhoff in his excellent investigation¹ arrives at the conclusion that the main constituent of cement clinker which forms the hydraulic hardening properties of Portland cement is a β bicalcium silicate enriched by dissolved lime. According to Dyckerhoff, the amount of lime dissolved in bicalcium silicate reaches 10 per cent. (estimated).²

Professor Dr. H. Kühl,³ who joins the ranks of Dyckerhoff's opponents, states that "a death blow was given to Dyckerhoff's theory when it was proved that free lime is definitely not present, even in a high lime clinker, provided it be

¹ Dr. W. Dyckerhoff, Ueber den Verlauf der Mineralbildung beim Erhitzen von Gemengen aus Kalk, Kieselsäure und Tonerde. Leipzig, 1925.

² *Ib.* pp. 77 and 92.

³ Prof. Dr. H. Kühl, Cement Chemistry in Theory and Practice, p. 23.

well burnt." But it is quite normal, when free lime is not detected in well-burnt cement, for this lime to be present in a solid solution in bicalcium silicate. A long continued heating to a temperature of 1,000 deg. C. sets lime free.

Little is known about the tricalcium silicate, but generally it is stated that tricalcium silicate dissociates at relatively high temperature. Shepherd and Rankin⁴ mention a temperature of 1,900 deg. C., other authors a lower one, but in any case a temperature of 1,000 deg. C. had been mentioned. The behaviour of Portland cement when heated leads one rather to accept Dyckerhoff's point of view.

The proportion of lime set free by heating and detected in various cements fluctuates between 9 and 11 per cent. The composition of the residue which remains after the digestion of lime set free in cement corresponds to the composition of a bicalcium silicate when one assumes that Al_2O_3 and Fe_2O_3 are combined with 3 CaO and 2 CaO respectively.

It was found that the presence of gypsum accelerates the secretion of CaO from the solid solution. This accelerating effect of $CaSO_4$ is difficult to explain, especially when it is taken into account that this process takes place at a temperature lower than the melting point of the substances reacted. It is possible that the accelerating effect of gypsum is connected with a diffusion of $CaSO_4$ into the solid solution of CaO in $2CaO \cdot SiO_2$. If this is the case it would be another example of reactions between substances in solid form, an analogy to the accelerating effect of CaF_2 on the reaction between $BaCO_3$ and SiO_2 at a temperature of 740 deg. C. when signs of melting had not been noticed.⁵

⁴ *Am. Journal of Science*, (4) 39 (1915).

⁵ Dr. W. Zander, *Zement*, 1931, No. 44, p. 953.

Swiss Cement Companies' Reports.

Soc. Suisse de Ciment Portland S.A., Basle (a holding company), has declared a dividend of 10 per cent. for the year 1931, when the net profit was 677,623 francs (£26,868). This compares with a dividend of 15 per cent. for 1930, when the net profit was 834,000 francs (£33,068).

Portland-Cementfabrik Laufen A.G. has declared a dividend of 5 per cent. for 1931, the same rate as for 1930.

Portland-Cementwerk Thaugen A.G., Schaffhausen, has declared a dividend of 8 per cent. for 1931.

United States Cement Companies' Reports.

International Cement Corporation gives its net income for the year ended December 1931 as 1,358,213 dollars, which compares with 4,539,509 dollars for 1930 and 4,950,433 dollars for 1929. There was a deficiency of 999,097 dollars for 1931 compared with a surplus of 2,009,611 dollars and 2,464,076 dollars for 1930 and 1929 respectively after paying dividends on the prior stock.

Alpha Portland Cement Co. reports a net loss of 907,773 dollars (£186,784) for the year ended March 31, 1932, compared with a net profit of 1,198,812 dollars (£246,669) for the previous year.

Pennsylvania-Dixie Cement Corporation shows a net loss of 1,455,699 dollars (£299,526) for the year ended March 31, 1932, compared with a net profit of 467,202 dollars (£96,132) for the previous year.

Cement Imports in Lithuania.

A bulletin issued by the Department of Overseas Trade on the Economic Conditions in Lithuania states that the cement imports into that country during 1931 were 87,994 metric tons at a cost of 6,796,600 lits (approximately £138,706).

The Kaiser Wilhelm Institute for Research on the Silicates.

At the forthcoming meeting of the Association of Friends of the Kaiser Wilhelm Institute for Research on the Silicates, a number of scientific and technical papers will be presented of which some of general interest are abstracted in the following paragraphs.

Tricalcium Silicate.

By Dr. Haegemann.

A joint research has been carried out with Dr. Quast to elucidate the hydraulic properties of tricalcium silicate, which can be prepared by prolonged heating somewhat below its melting point. The raw materials for the investigation were a very pure quartz sand and lime obtained by burning calcium oxalate. An intimate mixture in the molecular proportions $3\text{CaO} : 1\text{SiO}_2$ was first heated at $1,550^\circ\text{C}$. for three hours, at the end of which period it only contained 0.3 per cent. of uncombined lime. This was again burnt after renewed powdering and mixing. The uncombined lime was then only 0.1 per cent., while the Al_2O_3 and Fe_2O_3 present as impurities amounted to not more than 0.1–0.2 per cent.; i.e., an extremely pure tricalcium silicate was obtained.

The cementitious properties of this pure material were investigated. It satisfactorily passed the soundness tests; its initial setting time was five hours and final ten hours. Very small additions of various substances had the following effects on setting time. Accelerators: hydroxides, alkali silicates and carbonates, aluminium sulphate, alum, gypsum (more than 5 per cent.), the chlorides of calcium, magnesium and aluminium, and tricalcium aluminate. Retarders: borax, sugar, potassium bichromate, ferric and ferrous sulphates, manganous and zinc sulphates, ferrous and stannic chlorides, dicalcium ferrite and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$; Without effect: sulphates of the alkalis and alkaline earths. In contrast to the compounds of iron oxide, the compounds of alumina, with the exception of $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, are seen to accelerate setting.

The hardening of tricalcium silicate proceeds very slowly, and the tensile strength after 28 days combined storage is only 284.5 lb. per sq. in. The addition of 3 per cent. CaCl_2 increases this to 555 lb. The research confirms that tricalcium silicate is the cause of the hydraulic hardening of Portland cement, even though the pure compound $3\text{CaO} \cdot \text{SiO}_2$ hardens very slowly.

Reactions Between Water and Cement.

By Professor Kühl.

The new experimental methods used by T. Wang allow of the separation at any desired stage of the three substances present during hydration, viz., cement grit, liquid phase, and newly formed compounds. Analysis of these gives an insight into the equilibrium conditions in the liquid phase, into the chemical composition of the products of hydration, and into the progress of the reaction during the decomposition of the cement particles. In this way the formation of lime hydrate and tricalcium hydroaluminate was established. Along with these there is formed a hydrosilicate containing 2 molecules SiO_2 and 3 molecules CaO . The decomposition of the cement grains proceeds in stages: first the aluminates are dissolved and pass into solution, while a portion of the silicate forms a semi-permeable envelope around the cement particles. The reaction

proceeds extremely slowly and has only penetrated a distance of 6μ at the end of three months. H. Berchem has shown that the reaction is much more rapid with aluminous cement, and has penetrated 5μ at the end of one day. The hardening of aluminous cement is characterised by the fact that the liquid phase consists of lime water which is not even one-tenth saturated. With aluminous cement, in place of the tricalcium hydroaluminate formed with Portland cement, a dicalcium hydroaluminate having 8 molecules of H_2O is produced, which forms hexagonal crystals and has a very slight solubility, but one nevertheless ten times greater than that of tricalcium hydroaluminate. A leaching-out process also occurs during the hydration of aluminous cement, and in spite of the low SiO_2 content, an envelope of silica is formed of which the outer layers apparently consist of a hydrosilicate low in lime, or even of pure silica. F. Kämpfe has proved that the hydration of blast-furnace slags proceeds with absorption of calcium hydroxide. The access of the hydrate was brought about by means of milk of lime contained in a dialyser. The course of the reaction depends upon the sulphur content of the slag. The reaction takes place on the particle of slag, which absorbs lime and then gives rise to a process of colloidal swelling. The absorption of lime proceeds rhythmically inasmuch as a greater lime consumption sets in when a certain concentration is attained and proceeds so vigorously that the diffusion from the dialyser is unable to cope with it. The result is a great dilution of the lime hydrate in the liquid phase, a retardation of the reaction, and thus the rhythmic process.

The Zone of Ring Formation in a Rotary Kiln.

By Dr. H. E. Schwiete.

To remove a ring formed in a rotary kiln it was heated for a considerable time to a temperature of $1,800$ deg. C. ($3,172$ deg. F.). The ring consisted of variously coloured zones parallel to the wall of the kiln. The material on which the flame directly impinged was pure white. Thin sections of this white substance showed on microscopic examination the presence of xenomorphic crystals. The darker material was of idiomorphic structure in a bed of glass. The crystals were biaxial, monoclinic, or rhombic, and were frequently also of hexagonal structure. The white portion was carefully separated from the dark under a binocular microscope, and an optical analysis of the white material showed its refractive index to agree with that of tricalcium silicate. X-ray analysis also gave the same lines as tricalcium silicate. Chemical analysis gave the following percentage composition: CaF_2 3.2, $CaSO_4$ 1.39, $3CaO.SiO_2$ 87.53, and $3CaO.Al_2O_3$ 4.51. This composition accounts for 70.18 per cent. CaO , while the chemical analysis gave a total of 70.43 CaO ; the agreement is thus very close. It is thus found that tricalcium silicate has been formed from a normal raw meal containing CaF_2 as a flux, under the conditions present in this particular kiln, viz., high temperature for a prolonged period and a feebly reducing flame. Iron oxide and alumina were carried away to the cooler parts of the kiln.

A Damp Cupboard for Cement Testing.

In the description of the damp cupboard at the Imperial Institute in our June number, the figure "90 per cent." on page 213, line 7, should read "96 per cent." This is, of course, important, as it proves that the cupboard more than satisfies the requirements of the British Standard Specification for Portland Cement.

Cement Companies' Dividends.

French Cement Companies' Dividends.

Etablissements Poliet et Chausson has declared a dividend of 80 francs for the year 1931, with a net profit of 24,541,281 francs (£197,578). This compares with a dividend of 120 francs in 1930, when the net profit was 32,657,814 francs (£262,924).

S.A. des Chaux et Ciments de Lafarge et du Teil has declared a dividend of 69.10 francs on its "A" shares and 59.10 francs on its "B" shares for the year 1931, with a net profit of 22,615,193 francs (£182,072). The net profit for 1930 was 17,384,573 francs (£139,961), when the same dividends were paid.

Soc. Nouvelle des Chaux et Ciments H. de Villeneuve had a trading profit of 428,942 francs (£3,453) in 1931. The trading profit for the previous year was 574,721 francs (£4,627).

S.A. des Ciments Portland "La Desvroise" has declared a dividend of 150 francs for 1931, with a net profit of 2,007,905 francs (£16,165). This compares with a dividend of 275 francs in 1930 when the net profit was 4,452,383 francs (£35,845).

Soc. des Ciments et Chaux Hydrauliques du Nord has declared a dividend of 20 francs gross for the year 1931, against 45 francs gross for 1930.

S.A. des Ciments Portland Artificiels d'Origny-St.-Benoite has declared a dividend of 200 francs gross for the year 1931 compared with 300 francs gross for the year 1930. The net profit for 1931 was 6,022,907 francs (£48,489) compared with 12,013,333 francs (£96,717) for 1930.

Chaux Hydrauliques et Ciments du Vermandois showed a net profit for the year 1931 of 194,743 francs (£1,567), compared with 400,111 francs (£3,221) for 1930.

Soc. des Ciments et Chaux de Neufchatel reports a trading profit of 2,050,618 francs (£16,509) for 1931 compared with 2,769,002 francs (£22,292) for 1930. The cement sales increased from 38,805 tons in 1930 to 39,973 tons in 1931.

Soc. des Ciments Français has maintained its dividend of 250 francs for 1931. The net profit for 1931 was 17,967,836 francs (£144,656) compared with 17,262,595 francs (£138,979) in 1930. The output of cement was 673,423 tons in 1931 compared with 662,477 tons in 1930.

Indian Cement Company's Dividend.

The Indian Cement Company has declared a dividend of 6 per cent. for 1931, with a net profit of Rs. 4,26,751 (£32,014). The same dividend was declared for 1930, when the net profit was Rs. 3,84,087 (£28,813).

Spanish Cement Company's Dividend.

Sociedad General de Cementos Portland de Sestao has declared a dividend for 1931 of 7 per cent., with a net profit of Ps. 140,491 (£2,965). This compares with a dividend of 6 per cent. in 1930 when the net profit was Ps. 140,452 (£2,964).

Swedish Cement Company's Dividend.

Klagshamns Cementverks A/B reports a net profit of Kr. 148,539 (£8,183) for the year ended December 31, 1931, and a dividend of 6 per cent. has been declared.

Chemical Structure and Strength of Cements.

By DR. DESIDER STEINER.

In the article by Mr. O. F. Honus on "The Importance of Chemical Analysis in Determining the Rational Composition of Portland Cement," which appeared in CEMENT AND CEMENT MANUFACTURE for September, 1931 (page 992), the author attempts to show that conclusions relating to the strength of cements can be drawn solely by calculation of the tricalcium silicate content. He ignores, however, certain fundamental factors, and it is accordingly necessary to offer the following comments.

The factors which influence strength are well known to all occupied in the manufacture of cement. Unfortunately, however, there are no quantitative or accurate numerical data which take all these different factors into separate consideration during manufacture, so that they can afterwards be combined. It cannot therefore be predicted that from any given modification a definite change in strength may be expected. The vast amount of detailed knowledge accumulated in a hundred years of cement manufacture and decades of research is such that it would be very surprising if a simple relation between tricalcium silicate content and strength were obtainable for an arbitrary series of cements tested in a research laboratory. The result must naturally be just as negative as it would be if any other property—say, fineness of grinding—were chosen and an attempt made to evolve a connection with strength.

There are great fundamental differences in the various Czechoslovakian cements. They are obtained from different raw materials that can be opened up with varying degrees of difficulty. Both wet and dry processes are used, and both rotary and shaft kilns, with different degrees of burning. Raw meal and cement are ground to varying degrees of fineness and by different methods. Again, fluxes may or may not be used and the amount of gypsum incorporated in the cement is by no means constant. Even if we only consider the multiplicity of the chemical analyses it is more than risky to calculate strength solely from the calculated tricalcium silicate content. Cement literature, especially in Germany, is of late years so full of formulæ for cement, some of them very good, that a new and so difficult calculation will not receive the approval of either practical or theoretical workers.

In any attempt to discover relationships between chemical composition and strength, the first necessity is to maintain all other subsidiary conditions so far as possible constant. In this sense extremely instructive material is provided by close supervision of production in a single works using the same machinery throughout. The problem of the works chemist is then to produce cement of the best quality (*i.e.*, of the best strength and with otherwise good properties) by consideration of the chemical relations—let us say, if desired, by attaining the highest tricalcium silicate content—under the given conditions and with the given raw material without seriously increasing the production costs.

In the following I propose to give the calculations relating to a single example from the many at my disposal, and would suggest that similar calculations be carried out in other works with the object of comparing the numerical data with those here given.

New quarries were opened up to feed a wet-process rotary-kiln plant, and the problem arose of producing a thoroughly sound cement of the best quality from these raw materials without modifying the former conditions of manufacture and with the minimum correction. Numerous preliminary experiments showed

the best silicate modulus to be around 2.30, more particularly because this could be continuously maintained. A series of cements was burnt in the same rotary kiln, maintaining constant the raw meal fineness, water content of slurry, cement fineness, gypsum, etc. The degree of burning was in all cases excellent and no free lime was found in any of the clinkers. The analyses and crushing strengths of the resulting cements are given in Table I. The analyses show that the chemical differences mainly consist in gradations of silica and lime contents.

TABLE I

Clinker.		1	2	3	4	5	6
Percentage analysis without gypsum.	SiO ₂	23.16	22.38	22.76	22.06	21.64	21.50
	Al ₂ O ₃	6.72	6.40	6.36	6.08	6.12	5.80
	Fe ₂ O ₃	3.60	3.84	3.28	3.60	3.44	3.42
	CaO	64.56	64.90	65.46	66.38	66.62	66.54
	MgO	1.36	1.72	1.65	1.58	1.76	2.48
Lime modulus		1.92	1.98	2.02	2.09	2.13	2.16
Silica modulus		2.24	2.18	2.36	2.27	2.26	2.33
Crushing strength, lb. per sq. in.	3 days	2,986	4,053	4,622	5,119	5,546	5,716
	7	4,309	5,731	5,830	6,854	7,494	8,148
	28	5,475	6,328	7,110	8,532	8,674	9,030
	28 days' combined storage ..	6,826	7,721	8,432	9,527	9,741	10,281

Professor Kühl has recently introduced as a criterion of cement analyses a formula which is in good agreement with fundamental theory. This aims at a

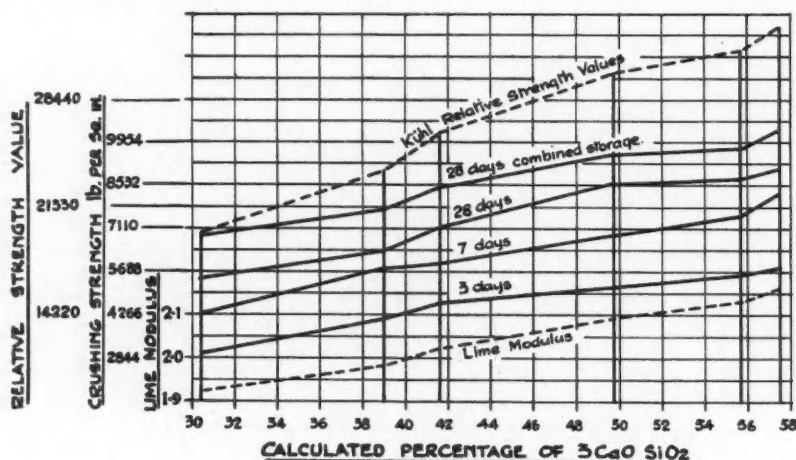


FIG: 1

cement composed as nearly as possible of the compounds $3\text{CaO}.\text{SiO}_2$, $3\text{CaO}.\text{Al}_2\text{O}_3$ and $2\text{CaO}.\text{Fe}_2\text{O}_3$. This lime saturation factor of Kühl, in percentages, is

$$\text{L.S.F.} = \frac{100\text{CaO}}{2.8\text{SiO}_2 + 1.65\text{Al}_2\text{O}_3 + 0.7\text{Fe}_2\text{O}_3}$$

This factor, calculated from the cement analysis, shows to what degree this ideal composition is attained. Sound cements of L.S.F. 90 and above must have been produced in a well equipped and controlled works and will have excellent strength.

Kühl has endeavoured to obtain a practical numerical criterion of strength. He defines this relative strength value as the sum of the crushing strengths at various dates and ten times the tensile strengths after the same periods of storage. This does not lay special emphasis on either form of test, but this may be done later in a revised definition.

The L.S.F. and the relative strength values (in this case limited to crushing strength) are compared below for Cements 1-6:

Cement.	1	2	3	4	5	6
L.S.F.	82½	85½	85½	89½	91½	92½
Relative strength value	19,596	23,833	25,994	30,032	31,455	33,175

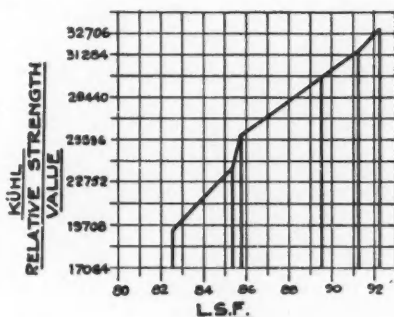


FIG. 2

The individual constituents of the cement can be obtained by means of this formula by first subtracting the CaO required for the Al_2O_3 and Fe_2O_3 from the total CaO, and portioning out the residual lime into tricalcium silicate and dicalcium silicate according to the following formula:

$$\begin{aligned} 0.263 \text{ Tri} + 0.349 \text{ Di} &= \text{SiO}_2 \\ 0.737 \text{ Tri} + 0.651 \text{ Di} &= \text{CaO} \\ \text{Tri} + \text{Di} &= \text{CaO} + \text{SiO}_2 \end{aligned}$$

$$\text{Tri} = \frac{349\text{CaO} - 651\text{SiO}_2}{86}$$

$$\text{Di} = \frac{737\text{SiO}_2 - 263\text{CaO}}{86}$$

The percentages of the individual constituents in our six cements may then be obtained by calculation:

Cement.	1	2	3	4	5	6
3CaO.SiO ₂ ..	30.3	39.1	41.7	49.8	55.9	57.4
2CaO.SiO ₂ ..	43.0	33.6	32.5	25.0	18.5	16.8
3CaO.Al ₂ O ₃ ..	17.8	17.0	16.9	16.1	16.2	15.4
2CaO.Fe ₂ O ₃ ..	6.1	6.5	5.6	6.1	5.9	5.8

These numerical data are incorporated in Figs. 1 and 2. It is seen that there is a fairly definite increase in strength when either the calculated tricalcium silicate content or the L.S.F. increases. Even in this extremely simplified case,

however, no definite relationship can be deduced. This is not surprising, since strength is in no way a property capable of rigid physical definition, but an arbitrary technical conception which does not even increase according to a definite law as the quantity of cement in the mix, or of any other hydraulic constituent, is increased. Further, it is by no means clear how the various compounds mutually affect one another in hardening, and finally, such great variations are possible in the production and cooling of the clinker minerals that their hydraulic properties are naturally unequal.

A more accurate calculation of the individual clinker minerals does not seem to be a practical possibility, since in general entirely hypothetical values are obtained. For example, if $2\text{MgO} \cdot \text{SiO}_2$ is taken into consideration in the calculations relating to Clinker No. 6, no dicalcium silicate is obtained, but only tricalcium silicate; further, free lime must remain over, which cannot, however, be detected analytically. From this point of view Cement No. 6 has far more than the maximum possible lime content. Commercial cements of hydraulic modulus 2.30 and above do, however, exist; thus there is a well-known Czechoslovakian high-strength cement of 2.25 lime modulus and 1.83 silica modulus. Hess has recently dealt with the maximum possible lime content in *Zement* (Nos. 40 and 41, 1931). He succeeded, by using burnt lime as a component of the raw meal, in producing cement of L.S.F. above 100, i.e., above the maximum given by the Kühl formula. Naturally all the lime is then present as tricalcium silicate, and in addition free lime must be present. Unfortunately he did not determine the free lime in his cements. His highest limed clinker gave the percentage analysis SiO_2 19.05, Al_2O_3 5.56, Fe_2O_3 3.22, CaO 71.17, MgO 0.50, with lime modulus 2.56 and silica modulus 2.16. This gave the following strengths in lb. per sq. in. for a 1:3 mix, the cement being ground to 6 to 8 per cent. on the 180 sieve, and fulfilling the Czech and German specifications.

		2 Days.	3 Days.	7 Days.	28 Days.
Tensile	355	350	370	384
Crushing	4,607	5,759	6,996	7,906

I was impressed by the fact that chemical analysis alone can give no complete picture of the clinker minerals, but must be amplified by petrographic examination, in the case of two technical cements from the same raw meal, both equally well burnt, but burnt in different kilns. The chemical analyses, fineness, etc., of the two cements were exactly the same, viz.:

		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Lime mod.	Silica mod.
Cement 1	21.52	5.90	3.50	66.58	2.44	2.15	2.28
Cement 2	21.50	5.80	3.42	66.54	2.48	2.16	2.33

Notwithstanding this the strengths differed fairly considerably:

		Crushing strength (lb. per sq. in) after				28 Days' combined storage.
		3 Days.	7 Days.	28 Days.		
Cement 1	5,261	6,783	8,603	9,670	
Cement 2	5,716	8,148	9,030	10,238	

Obviously the different conditions of cooling, or possibly different conditions during grinding, have had an effect. In any case this example clearly shows that extreme caution must be exercised in using chemical analysis in determining the rational composition of Portland cement.

Constancy of Volume of Portland Cement.

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ALTHOUGH, strictly speaking, there is no constancy of volume in Portland cement—since variation of moisture content, as well as heat and cold, will affect its volume—yet useful results are obtained from observation of pats of cement kept in moist air or immersed in water. In sound cement the difference in volume is not noticeable without the aid of scientific apparatus, and the value of the test for constancy of volume consists in ascertaining undue expansive tendencies.

The "soundness" of Portland cement is of paramount importance, and an accelerated test for soundness can be made with simple apparatus, which will be comparatively free from error due to the personal equation or to local sur-

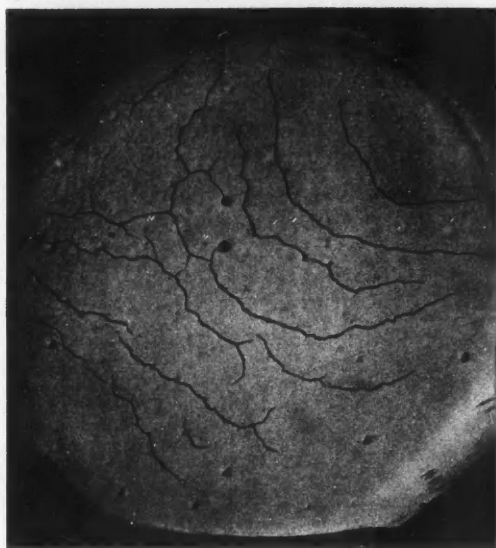


Fig. 1.

roundings. The test for soundness obviates the necessity for long-period tensile tests as a guide to this property of cements, and the result of the test is of more value. The accelerated tests most generally used are those in which a pat or block of neat cement is kept in steam or boiling water for a period.

Some rather surprising results are occasionally obtained from experiments on the soundness of cements. Contraction cracks in test pats (see Fig. 1), which sometimes occur during setting, are rarely a sign of bad quality. They are more generally found to be due to faulty manipulation rather than to any doubtful quality in the cement. The cracking arises from shrinkage caused by lack of humidity of the atmosphere, by rise and fall of the temperature in the test room, or by draughts of air passing over the pat whilst it is setting. Again, vibration of the

pat whilst the cement is setting may cause cracking similar to a contraction crack. Contraction cracks are also found if the test pats, when moist, are left in the sun or placed on a dry porous plate; excess of water in the gauging will also cause shrinkage or contraction. The difference in the appearance of cracks thus caused and those due to unsoundness will be seen from a comparison of Fig. 1 and Fig. 2.

The expansion of cements is generally caused by what is known as "free" or uncombined lime introduced into the product either by careless mixing or burning of the raw materials, or by the incorporation of under-burnt clinker.

If cement is poorly manufactured, aeration or atmospheric slaking will, to some extent, render inert any free lime present; but a properly manufactured cement will withstand the hot or boiling tests as soon as the material is taken from the grinding mills, and no special aeration is necessary.

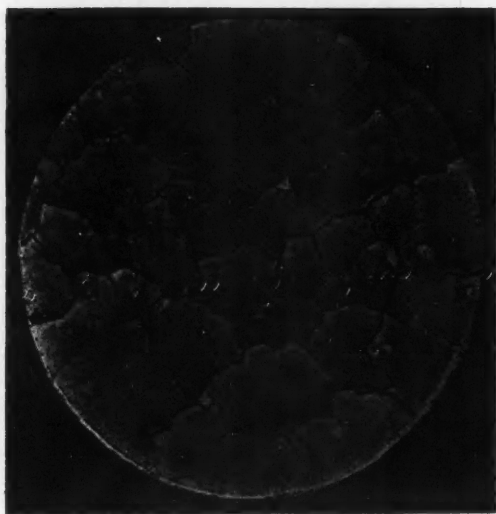


Fig. 2.

It cannot be stated with any degree of certainty that results obtained by the boiling test—the now general test for soundness—indicate those which may be experienced in construction work, but there is no doubt that if a cement is in the slightest degree unsound the hot test will at once detect and emphasise the weakness.

In the early days of cement manufacture, troubles were caused by expansion of the material through faults in the manufacture, which resulted in swelling and ultimate disintegration after the work was in place. An early device for the testing of over-limed or expansive cements was to mix a sample of the material with water to about the consistency of treacle, the whole being then poured until overflowing into a bottle or small glass test-tube, which was shaken and then placed aside in a cool place. If the cement was over-limed, or even if the grinding and amalgamation of the raw materials had not been properly carried out

by the manufacturer, the cement was expected to expand and split the glass sooner or later according to the degree of imperfection. If, on the other hand, the cement was under-limed (or over-clayed) it would contract and become loose in the receptacle. In this test care had to be taken to keep the bottles or tubes in a cool place and in an even temperature; for if they were placed in a warm atmosphere or near a fire cracking might result through the different rates of expansion of glass and cement even if the cement were perfectly sound. The test is not therefore to be relied upon.

Another simple test for the behaviour of cements is to make two small pats each about 3 in. in diameter by $\frac{1}{4}$ in. thick at the centre and diminishing to thin edges. The pats are gauged to a plastic paste and placed upon pieces of glass, and 24 hours afterwards one of them is immersed in cold water and the other left in a moist atmosphere. Both pats should be examined at regular intervals over a period of seven days, and the first indication of any disturbance or disintegration will be detected by the appearance of small cracks around the edges or extending from the centre of the pats. Other alterations of form may follow, such as lifting up at the edges or in the centre of the pat. Subject to the avoidance of contraction as explained earlier, good Portland cement will show no signs of cracking, scaling, crumbling or warping; nor, indeed, will it suffer any deviation of form whatever under this test. Any defect in the sample will first appear in the pat under water; but since it often happens that the evidences of unsoundness take a long while to appear, this method has given way to the accelerated or hot-water tests previously mentioned. The great value of these lies in the short time which elapses before indications of defects begin to appear.

Cements which stand the accelerated tests by steam or boiling water should be used in preference to others, for although hot tests may sometimes reject suitable material they will always reject a material unsound by reason of active expansion.

Pats can best be protected from evaporation until setting has occurred by storing them in a covered damp-box or under moist cloths. The formation of cracks due to shrinkage, which may be taken by the inexperienced to be due to expansion, is avoided by these means.

In the present state of knowledge it cannot be said that cement should necessarily be condemned simply for failure to pass the accelerated tests; nor can a cement be considered entirely satisfactory simply because it has passed these tests.

United States Tests for Soundness.

In the United States the terms of the Standard Specification for Portland cement in regard to the tests for constancy of volume are as follows:

"A pat of neat cement shall remain firm and hard, and show no signs of distortion, cracking, checking, or disintegration in the steam test for soundness. Note.—Unsoundness is usually manifested by change in volume which causes distortion, cracking, checking, or disintegration. Pats improperly made or exposed to drying may develop what are known as shrinkage cracks within the first 24 hours and are not an indication of unsoundness. The failure of the pats to remain on the glass, or the cracking of the glass to which the pats are attached, does not necessarily indicate unsoundness.

"A steam apparatus which can be maintained at a temperature between 98 and 100 deg. C. is recommended. The capacity of this apparatus may be increased by using a rack for holding the pats in a vertical or inclined position.

"A pat from cement paste of normal consistency about 3 in. in diameter, $\frac{1}{2}$ in. thick at the centre, and tapering to a thin edge, shall be made on flat, clean

glass plates about 4 in. square, and stored in moist air for 24 hours. In moulding the pat, the cement paste shall first be flattened on the glass and the pat then formed by drawing the trowel from the outer edge towards the centre, then flattening the top. The pats used for the time of setting tests by the Gillmore method may be used for soundness tests.

"The pats shall then be placed in an atmosphere of steam at a temperature between 98 and 100 deg. C. upon a suitable support 1 in. above boiling water for five hours. Note.—It is important that the specimens be 24 hours old when

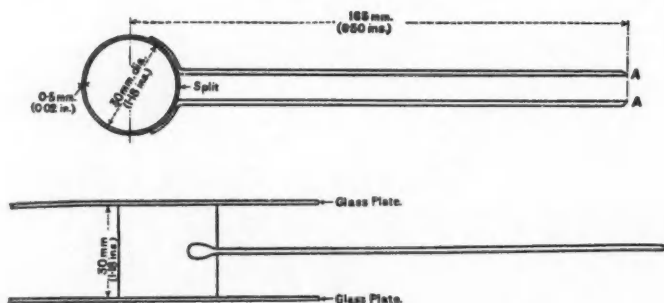


Fig. 3.

placed in steam, since variations in their age will produce differences in the results of the steam tests. Particularly noticeable are the effects of steaming pats too soon, for many specimens steamed when only 10 or 12 hours old give apparently satisfactory results while failure would be observed if they were not placed in steam until 24 hours old.

"Should the pat leave the plate, distortion may be detected best with a straight-edge applied to the surface which was in contact with the plate."

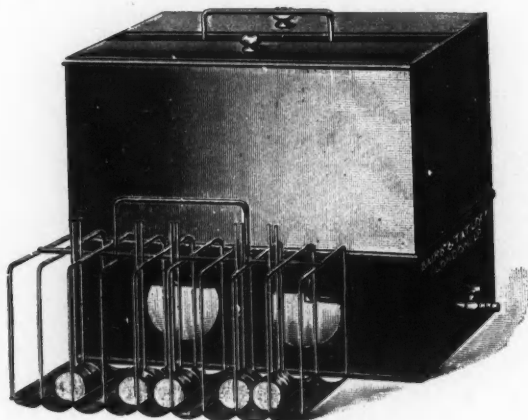


Fig. 4.

The Le Chatelier Test.

In the British Standard Specification for Portland Cement the soundness test specified is that known as the Le Chatelier test; the cement must not show a greater expansion than 10 millimetres when first tested, but if this is exceeded it may be spread out for seven days' aeration and must not then exceed 5 mm. expansion.

The apparatus for conducting the Le Chatelier test (Fig. 3) consists of a small split cylinder of spring, brass, or other suitable metal 0.5 millimetre (0.02 in.) thick, forming a mould 30 mm. (1.18 in.) internal diameter and 30 mm. high. On each side of the split are attached two indicators with pointed ends (A A), the distance from these ends to the centre of the cylinder being 165 mm. (6½ in.).

In conducting the test, the mould is placed on a small piece of glass and filled with cement gauged in the usual way, care being taken to keep the edges of the mould gently together while this operation is being performed. The mould is

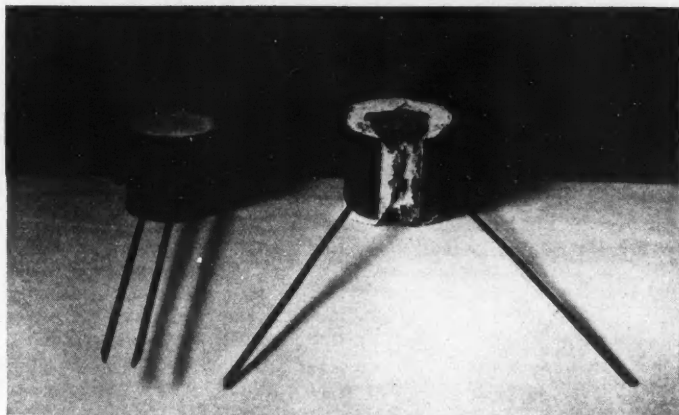


Fig. 5.

then covered with another glass plate, a small weight is placed on this, and the mould is then immediately placed in water at a temperature of 58 deg. to 64 degs Fahr. and left there for 24 hours. The distance separating the indicator point, is then measured, and the mould placed in cold water in a suitable receptacle, such as that shown in Fig. 4, which is brought to boiling point in 25 to 30 minutes and kept boiling for three hours. After cooling, the distance between the points is again measured; the difference between the two measurements represents the expansion of the cement, which must not exceed the limits laid down in the specification. Formerly the period of boiling was six hours, but long experience has shown that any expansion takes place within the first three hours and that the longer period serves no useful purpose. The contrast between a sound and an unsound cement under the test is illustrated in Fig. 5.

The test of expansion in Portland cement by the Le Chatelier method has been subjected to criticism from time to time on account of its alleged uncertainty, inaccuracy, or undue severity. This position has perhaps arisen on

account of the generally accepted idea that the results of cement tests by the Le Chatelier method show the soundness in actual work or otherwise of the cement under test. The basis of variance between the advocates and opposers of the Le Chatelier test has, so it is maintained, been the question as to whether any excess over the limited increase in volume permitted necessarily indicates the unsoundness or undesirability of a cement in practice; and not solely in the test itself, which is certainly a test for showing expansion pure and simple and not necessarily "unsoundness." So the test as applied to expansion alone will here be dealt with, since many cements which are sound in practice also show considerable expansion by this test.

It has been maintained by one writer that numerous Le Chatelier tests of cements suggest that the expansion shown on boiling is not always or necessarily due to free or loosely-combined lime, but may be due to changes in fine particles of an intermediate size (or clinker grit) under the influence of boiling water, and explanations are given of the theory of these changes. It has been suggested, too, that cements which have been ground from clinker which has been well and properly burned in the rotary kiln do not improve on aeration, but on the contrary may become expansive in volume. Others, again, have advocated that the total expansion by the Le Chatelier method in both cold and boiling water should be measured, the first measurement being taken as soon as the cement has set.

In following up these conclusions, and with a view to checking the results and the theories involved, prolonged investigations were instituted by the author with the result that the finding of increased expansion with aeration cannot be generally confirmed. It is shown that the behaviour of fresh and aerated cements in the Le Chatelier test are perfectly clear and unmistakable, and at once indicate the degree of expansion—but not necessarily unsoundness—of all cements tested by this method; and many curves have been prepared showing that while aeration may not always show a reduced expansion in a cement by the Le Chatelier method, it certainly does not show an increased expansion from the average results of a considerable number of tests.

For example, in the case of what may be called a sound cement, storing in bulk was found to reduce an expansion of 2.0 mm. to one of 0.5 mm. at 21 days, and to show no expansion in 28 days. The cement when spread out reduced in expansion to 1 mm. in three days, and no expansion was shown in the tests from seven days up to 28 days (Table I).

TABLE I.

	Fresh.	3 Days' Aeration.	7 Days' Aeration.	14 Days' Aeration.	21 Days' Aeration.	28 Days' Aeration.
	mm.	mm.	mm.	mm.	mm.	mm.
Cement in bulk	2.0	1.5	1.0	1.0	0.5	nil.
Cement spread out 1 in. thick	2.0	1.0	nil.	nil.	nil.	nil.

To ascertain whether the same results may be expected from a similar treatment of other cement, numerous additional tests have been carried out with further cements, and the aeration of these cements gives somewhat the same results by the Le Chatelier test as shown. Exceptions to this rule are very rare.

In considering the results of numerous and carefully conducted tests, it cannot by any means be admitted that rotary cement shows more expansion by the Le Chatelier test after a period allowed for aeration than it

does when fresh. As regards the question whether an underburned or well-burned clinker shows a greater or less expansion by the Le Chatelier test, the general experience is rather in favour of the reduction of expansion by harder burning.

Now, to come to the expansion under the Le Chatelier test which results from the division of cements into varying grades of fineness, such as (a) flour, (b) clinker grit, and (c) fine sieve residue, we have here three definite degrees of grinding which it is always interesting and instructive to make use of when examining any cements for expansion by this method. The amount of residue left on the standard 170-mesh sieve in sifting a cement by the standard method of testing for fineness will not exceed 10 per cent. of the quantity of cement tested. From the cement passing through the 170 sieve, the percentage of fine clinker grit in a cement may be collected by the use of a flourometer, which under a steady pressure of air separates the flour from the fine grit, and the percentage content of the latter can be accurately ascertained by weighing.

The percentages of "fine grit" and "flour" in cement necessarily vary according to the degree and process of grinding. A carefully carried out series of tests on two brands of cement showed that

(1) The two cements, showing respectively 2 mm. and 3.5 mm. expansion when fresh, were reduced in expansion after each successive period of seven days' aeration up to 35 and 28 days respectively, when the original expansion was again shown; but at 42 days in both cases this was reduced to 1.0 mm. and 1.5 mm.

(2) The expansion of the residue retained on the 170-mesh sieve with both samples was 25 mm. and 24 mm. when fresh and 24 mm. and 23 mm. after 35 days.

(3) The expansion of the fine cement passing through the 170 sieve was reduced upon aeration from 4.5 mm. and 2.75 mm., respectively, to 3.0 mm. and 1.0 mm. at 35 days.

(4) The expansion of the "flour" in one cement was reduced from 2.25 mm. when fresh to 2.0 mm. after 35 days, and in the other cement the flour expansion varied from 1 mm. when fresh to 2.0 mm. after 35 days' aeration.

(5) The expansion of the "fine grit" was also reduced upon aeration from 39 mm. and 21.0 mm. when fresh to 36 mm. and 7 mm., respectively, at the end of 35 days.

Thus the degree of expansion is greatest in the coarser residues and least in the finished cement and flour. It seems from these results that the presence of the flour, the preponderating element in the finished cement, to a very large extent, prevents serious expansion due to the grit in the combined sample as compared with the expansion measured when the grit alone is tested. The individual Le Chatelier test results of the component parts of Portland cement are interesting, therefore, only from the point of view of research.

Some variations occur from time to time in the results of tests by the Le Chatelier method as carried out by the same operator on the same cement, as is shown by the following schedule of the expansion in millimetres of a sample of cement divided into five sections and each sectional sample made up and tested at the same time but after varying periods of aeration. These variations, however, do not take the cement out of the class of a "sound" cement into that of an "unsound" one.

It will be found that the numerous investigations published from time to time by experimenters in connection with the Le Chatelier test clearly show the variations of this test with ordinary samples of cement and its dis-

LE CHATELIER EXPANSION TESTS ON ROTARY KILN CEMENT.

Sample of cement divided into five parts and aerated, tests being made every three days.

Period of Aeration.				Sample No. 1.	Sample No. 2.	Sample No. 3.	Sample No. 4.	Sample No. 5.
				mm.	mm.	mm.	mm.	mm.
As Ground	3.0	2.0	2.5	4.5	5.0
3 days	1.5	2.0	2.0	2.0	1.5
6 "	2.5	2.5	2.0	3.0	2.0
9 "	2.5	2.5	1.5	2.0	2.0
12 "	2.0	1.5	2.0	2.0	0.5
15 "	1.5	1.5	3.5	2.0	2.5
18 "	2.0	1.0	1.0	1.0	1.0
21 "	1.5	3.0	2.0	2.0	2.0
24 "	1.5	1.5	1.0	2.0	1.0

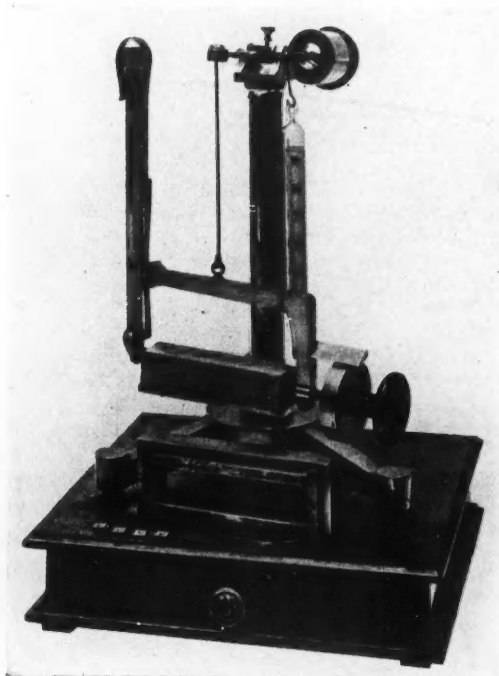


Fig. 6.

crepancies or idiosyncrasies. The result of each and every experiment is affected by

- (a) The nature of the raw materials used in the manufacture of the cement.
- (b) The process and plant used in the reduction and mixing of the raw materials from which the cement has been produced.

- (c) The chemical evaluation of the raw material mixture.
- (d) The method of burning the mixture, the plant employed and the fuel consumed.
- (e) The degree of final grinding of the clinker, and the plant employed.
- (f) The period of storing and aeration of the cement.
- (g) The personal equation in carrying out the test, the percentage of water employed, temperatures, etc.

All these points, with others, are of importance in calculating the value of the results of the Le Chatelier method of testing the expansion of cements. As far as can be seen, therefore, there can be no disputing this value, but whether the practical soundness of a cement is to be definitely gauged by these expansion results or not is a debatable point, and this doubtless is more the bone of contention—although not so clearly put forward by objectors—than the utility of the test itself.

It has been urged on the one hand that perfectly sound and satisfactory cements, which will make excellent concrete and will well withstand the test of age, may sometimes expand more than the 5 mm. allowed as the limit by the British Standard Specification; and, on the other hand, that many cements, which show little expansion by the Le Chatelier test, are inherently unsound. This in the main may be regarded as the arguments supporting the contention that this test is purely an expansion and not a soundness test.

The only practical difference in position, however, between the stringency of the Le Chatelier test and other boiling tests is that the 5 mm. expansion allowed by the British Standard Specification is a low limit compared with what has been found to be the expansion by the same test in many well-known and long-tried cements which have been used in considerable quantities with sound and satisfactory results.

But the demand for a limited expansion in cements eliminates products made by older and less exact methods and processes, and by the adoption of scientific methods and efficient plant there is no difficulty in producing a material which will come within the limits of expansion allowed by the British Standard Specification. In preparing a cement to pass this test, therefore, there would be no more effort required on the part of the manufacturer than in preparing one to pass the present Standard tensile strength test.

It cannot be disputed that this method puts the testing of the expansion (although not necessarily the soundness) of cements upon a distinct quantitative basis—an eminently desirable step. It is a test easily manipulated in comparison with the more elaborate Bauschinger bar test (Fig. 6) and which gives results readily calculated, clearly comparable, and at once declaring the cements most free from expansion, even if not the soundest; so long as the consumer desires to use a product possessing less expansive tendency than another, with other qualities equal, there is a distinct advantage to be obtained from its use.

Absence of expansion is the most essential quality for a cement to possess, and the ordinary rule-of-thumb tests for soundness as adopted by other specifications are the most inexact and the most dependent of all the routine tests upon personal judgment. Such a position as regards expansion the Le Chatelier test clearly avoids, and, finally, by ensuring absence of expansion alone this test has done much for the improvement in the quality of cements generally.

The "Cold Plunge" Test.

Soundness tests in some Portland cement specifications include the requirement that the cement shall pass the "cold plunge" or immediate immersion test, in terms of a clause such as the following: "Pats on glass shall show no sign

of contraction, expansion, or disintegration whether (1) after being kept in a humid chamber or in water for twenty-four hours they are placed in cold water which is then brought rapidly to boiling point and kept thereat for twelve hours, or (2) they are plunged in cold water shortly after being gauged and kept there for any length of time, or (3) they are kept entirely in moist air. The 'plunge' pats, in addition to not being cracked, warped, etc., must have a firm and permanent adherence to the glass."

"Unsoundness" in the cold plunge test is sometimes looked for in the cracking of the surface of a pat of cement which has been placed under water immediately after gauging, but more particularly in the distortion of the pat, which at times leaves the glass at the edges. This test is demanded only in rare instances and is less used to-day than formerly, and it is a test which many otherwise perfectly sound cements fail to pass. The scientific reason for so many cements showing surface cracking under this test is difficult to explain, except that it may be due to the action of water upon the scum or surface of the cement as it is setting. With slow-setting cements the cause of this surface cracking in the pats will probably be found to centre itself often, if not entirely, on mechanical action dependent upon the operator or the methods of carrying out the test. It cannot be definitely said that the test shows a defect in the cement, but it is certain that surface cracking is more often caused by the manipulation of the test than by any action of the cement under water. Indeed, from an experience of the vagaries of this test the defects shown by it appear to centre themselves in conditions quite outside soundness.

It has been assumed that cement containing gypsum will fail to pass the cold plunge test, but this is not so. Such an explanation has probably been put forward from time to time to explain the idiosyncrasies of the test, but it is better to admit the necessity for an inquiry than to base an explanation upon guesswork. Cements containing as much as 3 per cent. of gypsum will pass the cold plunge test, while cements which do not contain gypsum will show "skin" cracking and will lift off the glass. It is true that cements containing gypsum sometimes fail in this test, due perhaps to their slow-setting nature, and also because of the light fine particles of gypsum and cement brought to the surface by trowelling and shaking the pat whilst it is in preparation, but from many experiments it seems more reasonable to conclude that the treatment of the pat has more to do with the cracking under the cold plunge test than has the presence of gypsum, although this does not apply to the buckling of the pat.

It has also been observed that the temperature of the water into which the cement pat is plunged is sometimes the cause of surface cracking by this test. For instance, a number of pats immersed in water at a temperature of 66 deg. F. will be found to be sound by the cold plunge test, while the same cement made into pats will lift and crack on the surface if put into water at a temperature of 45 deg. to 50 deg. F.; it has also been noticed that in the case of two pats of the same cement, prepared in exactly the same way, if one is put under fresh water and the other under the older and alkaline water contained in the usual briquette tray, the latter pat will remain sound while the former is unsound.

Further, the soundness or unsoundness of a pat under this test is controlled to a large extent by the time elapsing between the finishing of the preparation of the pat and the time it is plunged under water. The same cement made into two pats may act as follows under this test: One pat, put immediately under water as gauged, will show surface cracking, while the other pat, if allowed before immersion to get a dull surface after some fifteen to twenty minutes in the atmosphere (a condition showing that the initial set is likely to take place

within the next fifteen minutes), may remain perfectly sound when immersed in water. On the other hand, exactly the reverse may happen.

The pats may also be affected by vibration of the water in which they are immersed. For instance, if the tank of water remains perfectly still and the water is not interfered with, a sound pat will often result, whilst another pat of the same cement, if placed in a tank where briquettes or other pats are being taken from or put into the water whilst the cold plunge test is setting, will show disintegration of the surface. Sometimes, again, if a prepared sample of cement is made into two pats, and one of them be shaken down and the surface trowelled, this one will crack in the cold plunge test, while the other sample of the same cement made into a pat by merely cutting into shape with a trowel, and no trowelling on the face, will be perfectly sound under the cold plunge test. This result of trowelling is seen in a more aggravated form in some cements either as briquettes or pats. In such cases it is noticed that the "skin" or "scum" on the surface will separate if there has been much trowelling, while if there has been no trowelling the surface will remain perfectly sound. This again is clearly distinguishable from the cold plunge test crack, and if a scientific explanation were wanted, the defect might be attributed to the action of sulphur compounds from the added gypsum which exists in greater quantity in the skin than in the body of the cement pat. This the author has demonstrated by experiment with successive small additions of gypsum to different cements, when it was found that ultimately in the majority of cases a time was reached when the skin of a shaken or trowelled pat or briquette would part from the body when placed in water after setting.

In observing the cold plunge pat test, therefore, important regard should be paid to the results from the trowelling of the surface of the cement pats, for a distinction can always be made between a cracking caused by over-trowelling and cracking caused in other ways. It will sometimes be seen that with a freshly made well-trowelled pat the skin will be denser, and water will find its way through this skin whilst the cement is setting and cause it slightly to lift in so doing and thus separate from the body of the pat in which the movement caused by infiltrating water would be much smaller. From other observations made in this direction it appears that the difference between the cracks observed on untrowelled pats under the cold plunge test and those on pats which have been over-trowelled is that in the former a somewhat general but slight surface disturbance takes place resulting in fine cracks on the surface of the pats, but with the over-trowelled pats a thin skin is seen on the top of the pat and this alone disintegrates whilst the pat itself remains sound and hard.

In summarising the author's experience of this test, it would appear that as a broad general rule only slow-setting cements are affected by the cold plunge test, and this without the quality of the cement being called into account. It is clear, however, that under this test defects might be separately or collectively occasioned by

- (a) The result of the fineness of grinding of the raw material used in the manufacture, and either high or low lime content.
- (b) The degree of burning of the clinker.
- (c) The percentage of gypsum added to control the setting of the cement.
- (d) Over-trowelling of the test pat in preparation.
- (e) The difference between the temperature of the cement when tested, and of the water when the pat is "plunged."
- (f) The period of aeration and temperature of the cement after grinding.
- (g) The method and treatment of the pats before and after "plunging."

An examination of the causes of surface cracking in the cold plunge tests shows that, from the results of a considerable number of tests, the cause of this cracking may be accounted for in one or other of the defects already noticed or by a combination of them.

After the pat has been under water for a time it is often taken out of the bath to see what has taken place; this repeated motion of the pat and water seems to set up a disturbance of the surface skin and so cause it to crack. Then, again, there is a personal element with this test which can make it either satisfactory or otherwise without any obvious difference in the method of carrying out the test. In some cases, also, some pats when placed in water immediately after gauging remain perfectly sound, whereas pats of the same cement if kept until the initial set has taken place show decided cracking on the surface and lifting.

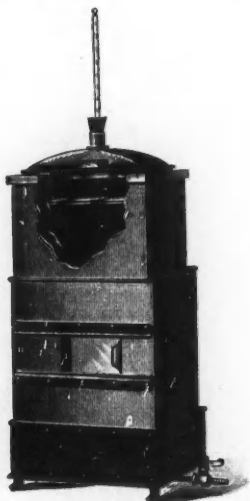


Fig. 7.

These are some of the points which throw doubts upon the practical utility of the cold plunge test, and the results go to prove that the test is even more subject to extraneous conditions than most other cement tests. It must therefore be held that, although a pat may crack and flake on the surface under this test, it does not by any means follow that the cement is unsound, as there is a possible doubt as to whether the handling of the cement or the cement itself, apart from the possibility of the defect being calculable or not, is the cause of the peculiarity. The value and results of the test are equally unimportant so far as experience in practice is concerned.

It may be said that an explanation of the behaviour of cements by these tests is that the surface contents of the pat differ in composition and constitution from the bulk contents (an experience not found in the practical uses of cement), and that whether a cement contains gypsum or not has little bearing upon the results by this test. A point in regard to the opinion sometimes expressed that faulty results by the cold plunge pat test essentially show a faulty cement, is

that when the test is carried out with a small amount of sand or other admixture the defect shown in the neat cement does not occur. Neat tests for tensile strength are hopelessly condemned as not representing the true qualities of the product, and they are not according to experience in practice; and so in the cold plunge test the neat cement results are a doubtful indication of the quality of the product under investigation.

Faija Soundness Test.

A well-known test for soundness of cement is that called the Faija test. It consists in subjecting a freshly gauged pat of cement to a moist heat of 100 deg. Fahr. for six or seven hours, or until thoroughly set, and then immersing it in warm water at a temperature of 115 to 120 deg. Fahr. for the remainder of the 24 hours. This accelerated test is based on the principle that moist heat accelerates the setting of cement, and that if it is judiciously applied the age of several days may be artificially given to a cement in a few hours. A sound cement acquires great hardness in a short time when treated in this way, but an unsound one, or one that would under ordinary conditions "blow" when used in work, is caused to develop this latter characteristic in a few hours; hence by the use of this test a definite opinion may be formed as to whether or not a cement is a safe one to use, independently of its tensile strength which may or may not be equal to that required.

The apparatus consists of a covered vessel, illustrated in Fig. 7, in which water is maintained at an even temperature of from 115 deg. to 120 deg. Fahr.; the space above the water is therefore filled with rising vapour and is at a temperature of about 100 deg. Immediately the pat is gauged it is placed on the rack in the upper part of the vessel, and in five or six hours it may be placed in the warm water and left therein for nineteen or twenty hours. If at the end of that period the pat is still fast to the glass, or shows no sign of "blowing," the cement may be considered perfectly sound; should any signs of blowing appear the cement is spread out in a thin layer for a day or two and a second pat made and treated in the same manner.

Another and perhaps readier test for soundness is as follows: Prepare sample pats of cement in the ordinary way, and after 24 hours in moist air, place them in a receptacle of cold water which should then be heated gradually to boiling point and allowed to boil for three hours. If the pats are sound the cement will be thoroughly satisfactory in constructional work in so far as freedom from expansion is concerned. This is, of all accelerated tests for soundness, the simplest and most convenient for the user to apply.

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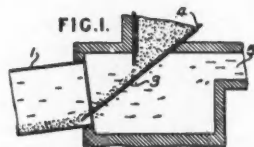
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Recent Patents Relating to Cement.

Portland Cements.

ANDREAS, A., 3, Engelstrasse, Munster, Westphalia, Germany. Sept. 1, 1930. No. 26111.

In the manufacture of cement, etc., the wet or dry raw material, e.g., slurry, is preliminarily treated before being fed to the kiln or sintering furnace by passage over a gas-permeable device through which the waste kiln or furnace gases pass, thus abstracting the dust from the gases and utilising the heat of the gases to calcine partially or wholly the raw material. The material is spread on or at the gas-permeable device in such a manner that its par-



ticles change their relative positions during their forward movement to the kiln. The fine grains or powder in the raw material may be screened off before the material is supplied to the gas-permeable device or the raw material may be first subjected to a balling, granulating or moulding operation or both screened and granulated. The figure shows one form of apparatus in which the raw material from a hopper 4 flows to a rotary kiln 1 by gravity over a stationary screen 3 through which the waste gases pass to an outlet 5. The screen 3 may be adjustable as to inclination. Other forms of apparatus are shown and described.

The specification comprises an apparatus having a travelling grate delivering the raw material into the kiln through a rotatable shoot. This apparatus is not described in the specification as accepted.

Portland and like Cements.

No. 368,812. BASSET, L. P., 54, Avenue Marceau, Paris. September 27th, 1930.

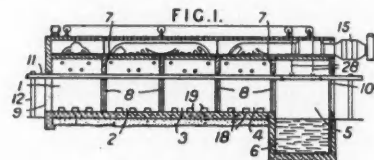
In a process for producing simultaneously iron or other metals and Portland cement or hydraulic lime, sufficient lime, and if necessary other ingredients such as silica or alumina, is added to the ore to give the slag the desired composition. The charge is ground to a fine powder and introduced into a rotary furnace which is heated by the combustion of pulverised fuel with the proportion of air required to obtain a carbon monoxide content of the furnace gases sufficient to prevent re-oxidation of the

metal and without fusion of the charge. The products leaving the furnace are cooled in a cooler and crushed, and the iron is removed by a magnetic separator.

Cement.

BRIGHENTI, G., 10, Rue Franklin, Lyons, France. Feb. 11, 1931. No. 4,330.

Artificial stone with a basis of cement and sand is made very hard by adding to the mixing water a solution of ferric chloride of about 20 per cent. strength and slowly drying the product by passing through a series of hot chambers, with a final bath



AIR DRYING MACHINE.

in molten sulphur. An apparatus to carry out the process consists of a series of chambers 1 . . . 5, the last containing a bath of molten sulphur 6. Hot air is passed to chamber 4 from the heater 15, and thence to chamber 3 by conduits 18, 19, and finally from chamber 2 to chamber 1 by conduits at the bottom. A cage running on a rail, 11, conveys the material through the chambers. In chamber 5 the cage is lowered by chains 28 from a winch into the bath of sulphur 6. Heat insulating doors 9, 10 are at the front and end of the apparatus, partitions 7 and doors 8 are between each chamber. Supports 12 for the rail 11 are of unequal height to allow for an inclination of the rail from the front to the end of the apparatus.

PATENTS.

The Proprietors of British Patents No. 275,463 for "Improvements in or relating to the Treatment of Carbonate Materials," and No. 269,480 for "Improvements in or relating to methods of and apparatus for treating materials" desire to introduce their inventions to the notice of manufacturers and others with a view to the inventions being worked commercially under licence or otherwise. All communications to be addressed to Jensen & Son, Chartered Patent Agents, 77, Chancery Lane, London, W.C.2.

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R. J. & A. R. PITCHERS,**ROCK PLACE,****GODALMING.****Cement Imports into Ceylon.**

In a bulletin issued by the Department of Overseas Trade giving a survey of the import trade of India and Ceylon for the year April 1, 1931, to March 31, 1932, it is stated that the quantity of cement imported into Ceylon in the year 1931 was 25 per cent. less than in the year 1930. Imports from the United Kingdom decreased from 38,300 tons to 25,000 tons, and those from Germany from 14,650 tons to 4,600 tons.

The quantity imported from Japan increased from 3,000 tons in 1930 to 12,350 tons in 1931. These figures compare with 1,000 tons in the year 1929 and 250 tons in the year 1928. The value of the imports from Japan in 1931 was Rs. 324,870. Cement imports of a value of Rs. 94,336 were also received from Denmark in the year 1931. The United Kingdom supplied approximately 61 per cent. of the value of the total cements imports in 1931, and Japan supplied 19 per cent.

A summary of the total imports of cement for the last five years gives the following figures: 68,200 tons (value Rs. 2,799,035) in 1927; 79,775 tons (Rs. 3,193,648) in 1928; 80,442 tons (Rs. 3,215,561) in 1929; 64,989 tons (Rs. 2,601,144) in 1930; 47,638 tons (Rs. 1,693,052) in 1931.

Cement Imports into Angola.

In a report issued by the Department of Overseas Trade on the economic conditions in Angola (Portuguese West Africa), it is stated that the quantity of cement imported into that province has averaged roughly 10,000 tons during the last few years. Belgium is the chief source of these imports, and contributed 2,894 tons (value £9,549 approximately) in 1926 and 3,791 tons (£10,521) in 1927. This compares with 2,709 tons (£6,876) and 3,373 tons (£9,693) contributed by the United Kingdom in the same years. The figures for Belgium in 1928 were 6,119 tons (£17,937) and for the United Kingdom 3,400 tons (£9,693). Germany and Portugal respectively contributed 1,455 tons (£4,941) and 1,411 tons (£8,064) in 1926, 2,611 tons (£2,718) and 314 tons (£900) in 1927, and 1,468 tons (£4,923) and 40 tons (£135) in 1928.

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Czechoslovakian Cement Companies' Reports.

Podoler Zementfabrik A.G. (Bohemia) has declared a dividend of 6 per cent. (Kc. 24) for the year 1931, with a net profit of Kc. 462,014 (£2,812), compared with a dividend of 14 per cent. (Kc. 28) in 1930 when the net profit was Kc. 508,363 (£3,094). The value of a share has increased from Kc. 200 in 1930 to Kc. 400 in 1931.

Königshofer Zement-Fabrik A.G. has declared a dividend of 40 per cent. (Kc. 80) for the year 1931, with a net profit of Kc. 22,024,000 (£134,047). The net profit in 1930 was Kc. 27,645,000 (£168,259) when a dividend of 50 per cent. (Kc. 100) was paid.

It is reported that the cement sales in 1931 of the Königshofer Zement-Fabrik A.G., which controls an output of 1,000,000 tons of cement in Bohemia, Germany and Austria, as well as brick and lime plants, were scarcely 6 per cent. below those in 1930.

Mährische-Slovakische Zementfabrik A.G. has declared a dividend of 6 per cent. for the year 1931, with a net profit of Kc. 406,444 (£2,473). The net profit for 1930 was Kc. 458,056 (£2,787) when the dividend was also 6 per cent.

Belgian Cement Companies' Dividends.

S. A. Ciments de l'Escaut has passed its dividend for the year 1931. The net profit for 1931 was 1,138,445 francs (£6,505) compared with 4,476,176 francs (£25,578) in 1930, when the dividend was also passed.

S. A. des Cimenteries et Briqueteries Reunis reports a net profit of 13,179,320 francs for 1931 compared with 22,671,135 francs for 1930. A dividend of 60 francs gross was paid in 1930, and no dividend was paid in 1931.

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Avery, W. & T., Ltd.	viii	Humboldt Deutzmotoren	vi
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Chemisches Laboratorium für Tonindustrie	—	Metropolitan-Vickers Electrical Co., Ltd.	xii
Constantin, E., Ltd.	xix	"Miag" Mühlenbau und Industrie, A.-G.	vii
Crompton Parkinson, Ltd.	—	New Conveyor Co., Ltd.	xx
Curtis, A. L.	—	Newell, Ernest, & Co., Ltd. . .	Front Cover
Davidson & Co., Ltd.	xxi	Pearson, E. J. & J., Ltd.	265
Davison, Charles, & Co., Ltd. . .	xvii	Pitchers, R. J. & A. R.	267
Diamond Lubricating Co., Ltd. . .	x	Polysius, G.	v
Dowdings, Ltd.	xxii	Renold & Coventry Chain Co., Ltd.	—
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Ewart Chain Belt Co., Ltd.	—	Rolland, John, & Co.	xvi
Fellner & Ziegler	ix	Ross Patents, Ltd.	xi
Firth, Thos., & J. Brown, Ltd. . .	xx	Ruston-Bucyrus, Ltd.	xviii
Fraser & Chalmers Engineering Works	—	Ruston & Hornsby, Ltd.	—
Frère, R., & F. Evrard	—	Sack Machinery Co., Ltd.	vii
Fuller Company	xix	Smidth, F. L., & Co., Ltd. . . .	ii, iii
General Electric Co., Ltd.	—	Taylor, J. Darnley, & Co., Ltd. .	ix
Glover, W. T., & Co., Ltd.	iv	Tonindustrie, G.m.b.H.	—
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Halspebe, Ltd.	vi	Visco Engineering Co., Ltd. . . .	—
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